LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-CONF-203081

Water Under Extreme Conditions

N. Goldman, L. Fried

March 22, 2004

227th Annual American Chemical Society Meeting and Exhibition
Anaheim, CA, United States
March 28, 2004 through April 1, 2004

Water Under Extreme Conditions

Nir Goldman and Larry Fried

LLNL

4/1/04

Water at High Pressure and Temperature

- Temperatures up to thousands of K
- Densities: 1.57 g/mL to 3.0 g/mL,
- Pressures up to 100 GPa
- Novel properties predicted, including superionicity, rapid dissociation

Planetary Interiors

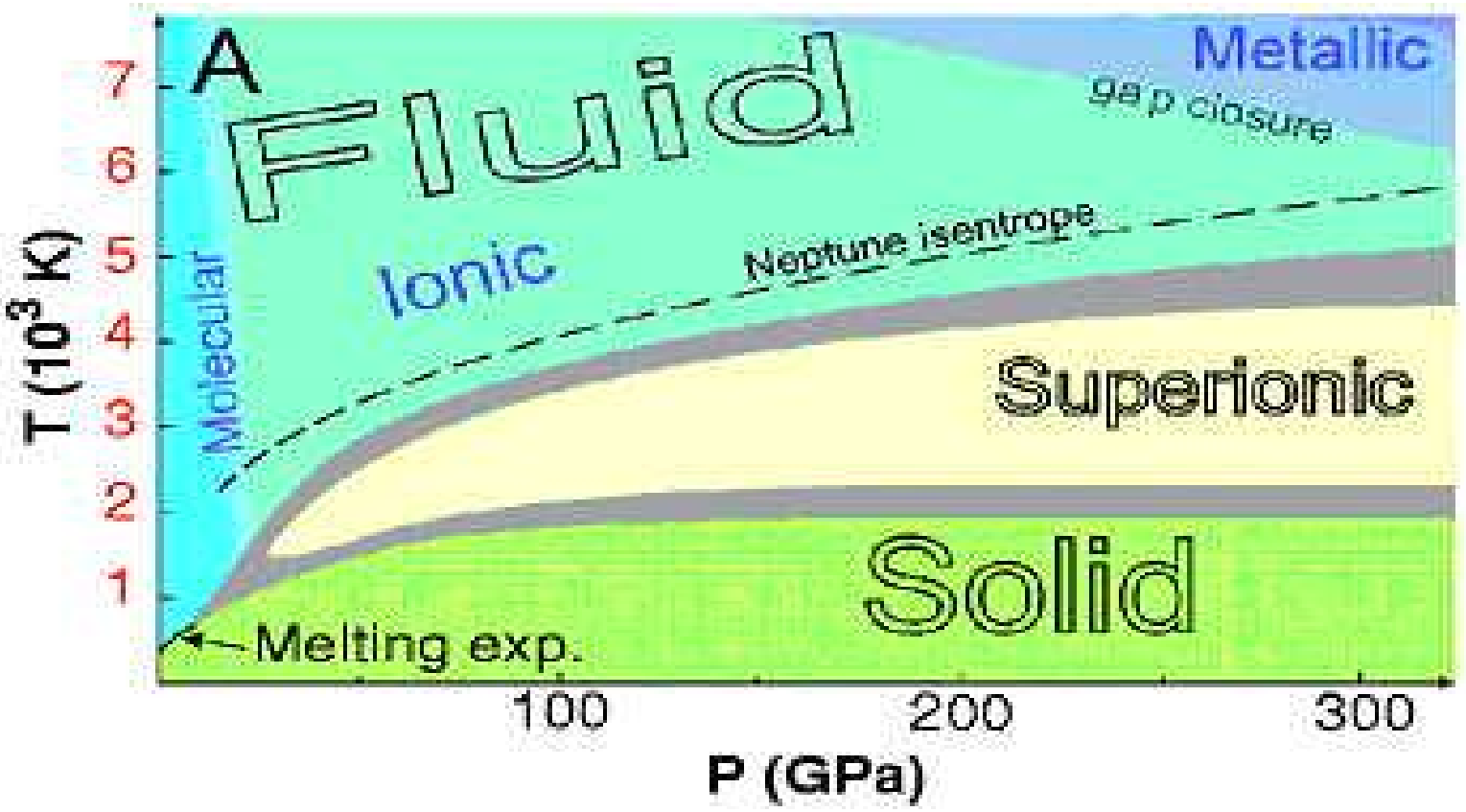
- Uranus, Neptune: 56% H_2O, 36% CH_4, 8% NH_3
- “hot ice” mixture contributes to magnetic field measurements by Voyager 2 spacecraft
- Due to high electrical conductivity, possibly from completely ionized H_2O

Cavazzoni et al., Science, **283**, 44, 1999.

Ab initio molecular dynamics

- NPT simulations with Carr-Parrinello molecular dynamics (CPMD)
- Small system size: 32 H_2O
  - pressure set to 30-300 GPa
- Temperature ramped from 300 to 7000K
- "Superionic" phase has oxygen lattice
  - D_H (2000K, 30 GPa) = 1.8 x 10^{-3} cm^2/s

Water phase diagram



Cavazzoni et al., Science, **283**, 44, 1999.

Superionic Phase controversy

- CPMD results with 54 H_2O do not show mobile protons or oxygen lattice[1].
  - shortlived H_3O^+ and OH^- pairs
- Experimental results:
  - No visible oxygen atom lattice[2].
  - Speciation is H^+, OH^-[3].

1. Schwegler et al., PRL, **87**(26), 265501-1, 2001.
2. Katoh et al., Science, **295**, 1264, 2002.
3. Chau et al., J. Chem. Phys., **114**(3), 1361, 2001.

Mending controversy

- CPMD *ab initio* MD software
  - Allows us to study structure, ion dynamics, and bond dissociation in exotic regions of phase diagram
- Revisit Cavazzoni et al. calculations,
  - larger system size
  - more detailed analysis of ion dynamics and bond dissociation

CPMD details

- Used version 3.82
- BLYP gradiaent corrected exchange correlation energy functional
- Troullier-Martins pseudopotential

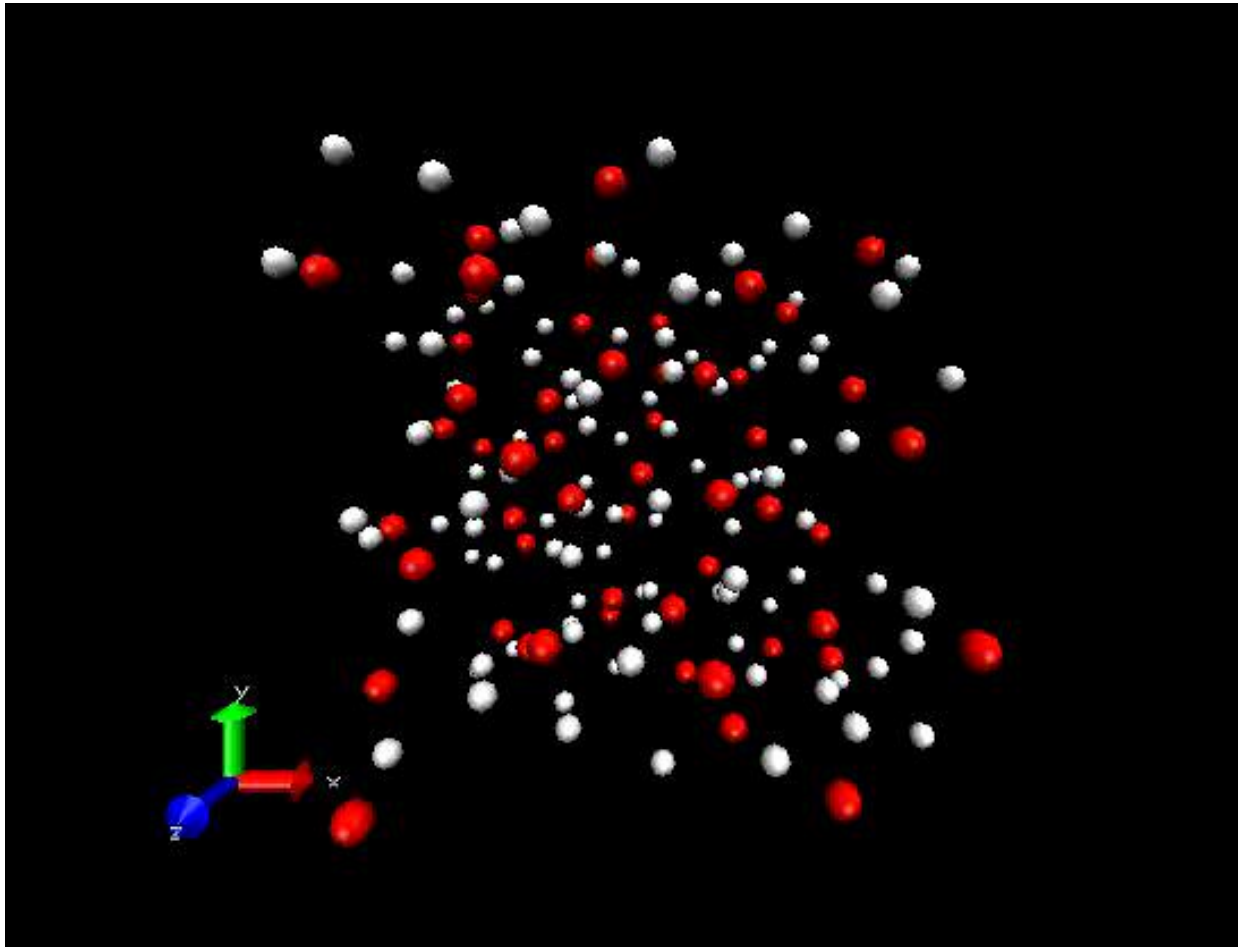
Simulation details

- 54 H_2O molecules
- Simulate along 2000K isotherm
  - 1ps equilibration, followed by 1-4 ps with Nosé-Hoover thermostats
- Density varied from 1.57 – 3.00 g/cc in steps of 0.2 g/cc
- Electron mass of 200-400 au
- Time step of 2-4 au

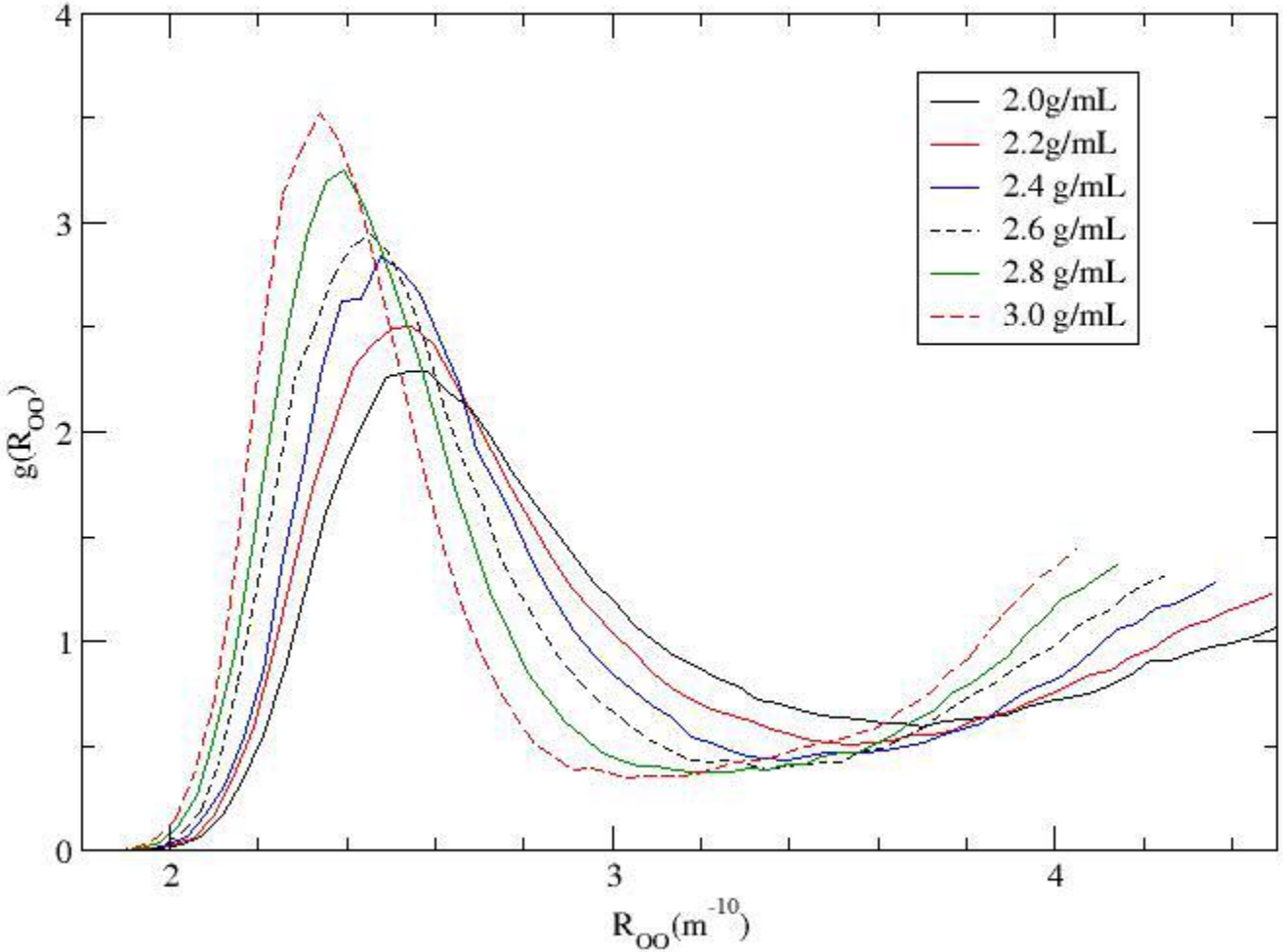
Game plan for “extreme” water simulations

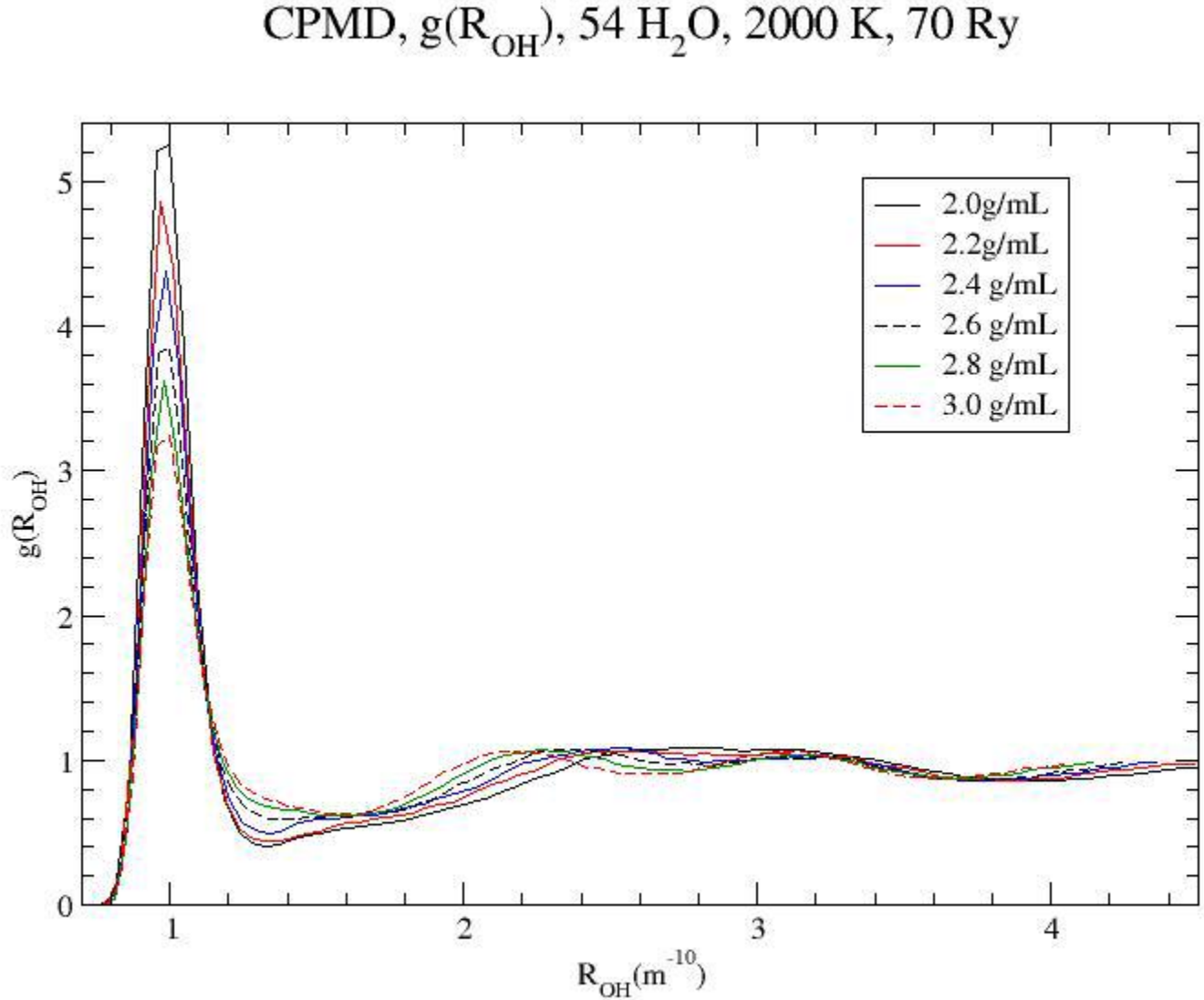
- Use CPMD to generate 1.0 – 3.0 ps long trajectories at 2.0 – 3.0 g/cc, 2000K
- Calculate $g(R_{XX})$, diffusion constant, $\langle C_{vv}(t) \rangle$
- Determine OH bond lifetime and similar kinetic functions

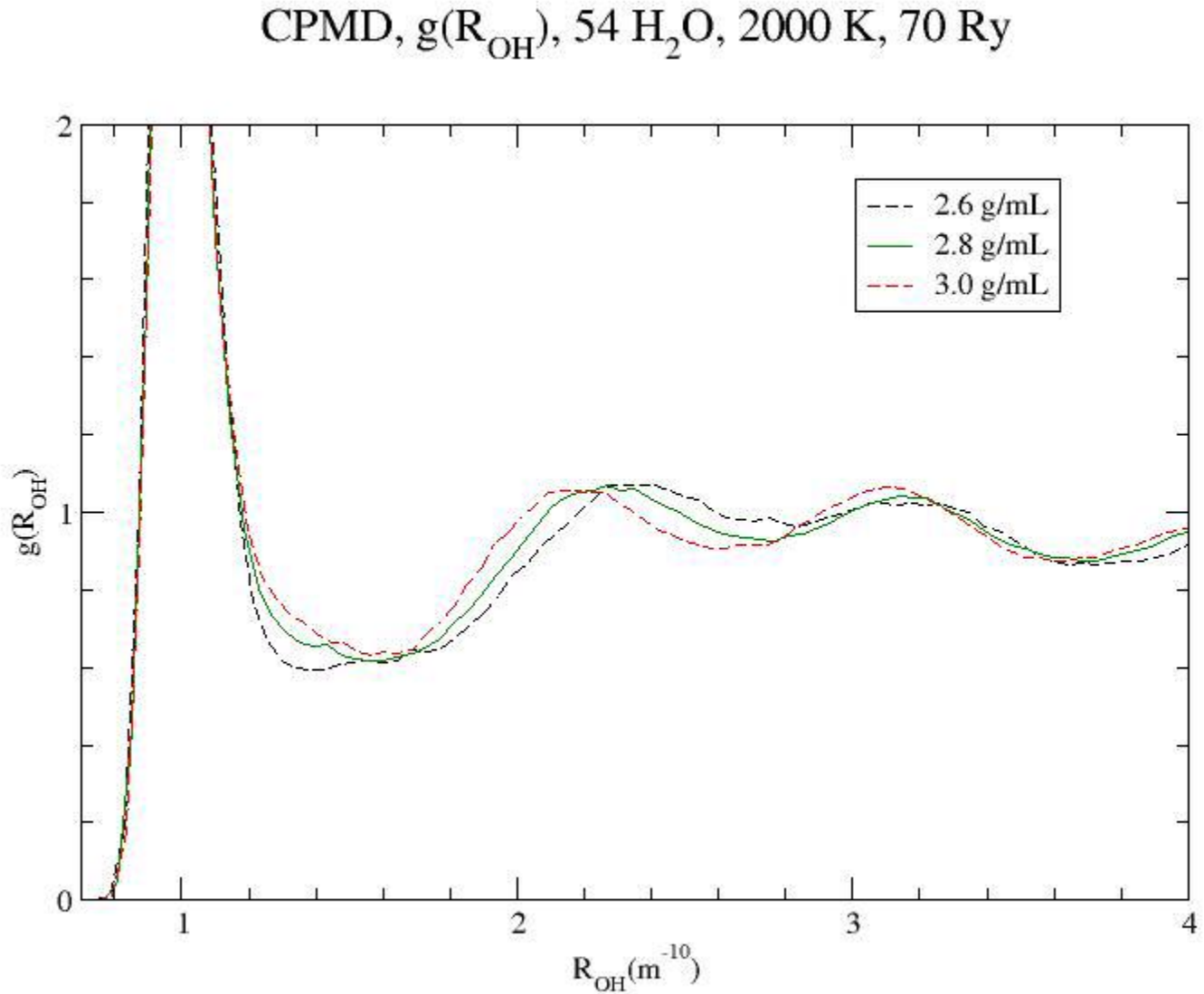
2.4 g/cc, 2000K

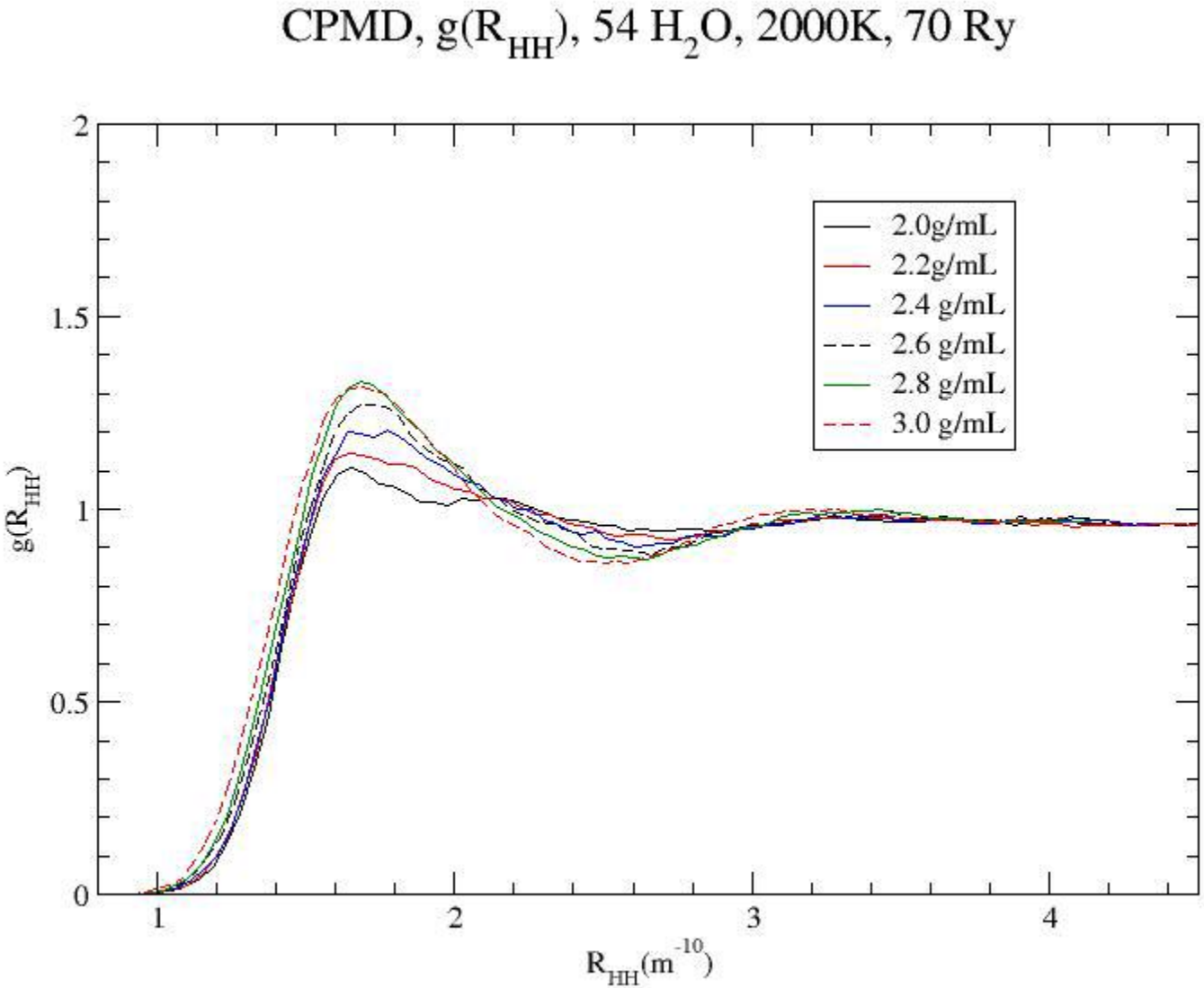


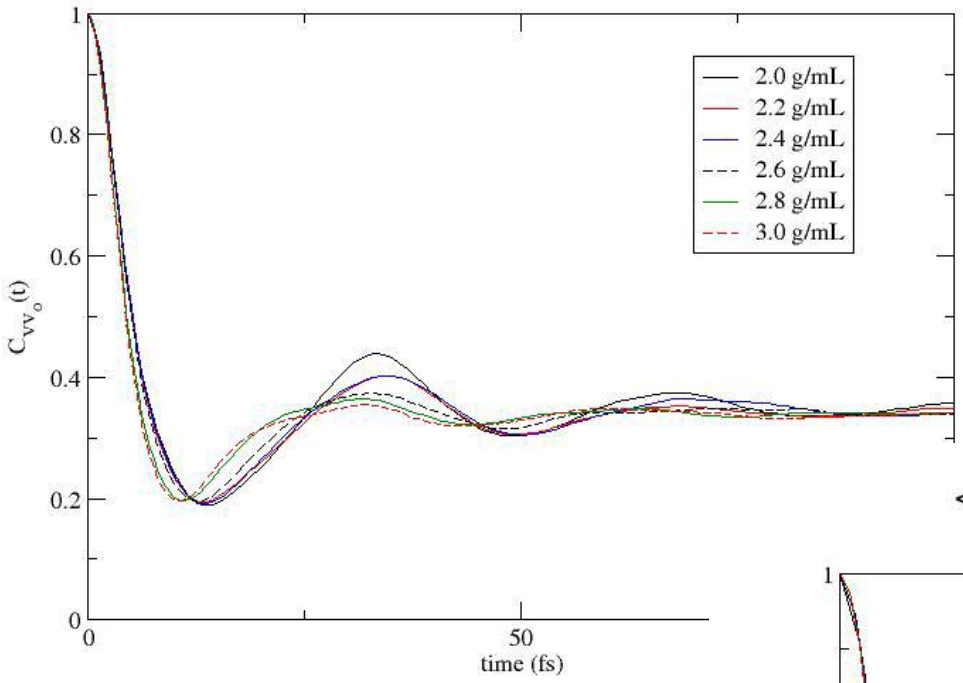
CPMD, $g(R_{OO})$, 54 H_2O, 2000K, 70 Ry

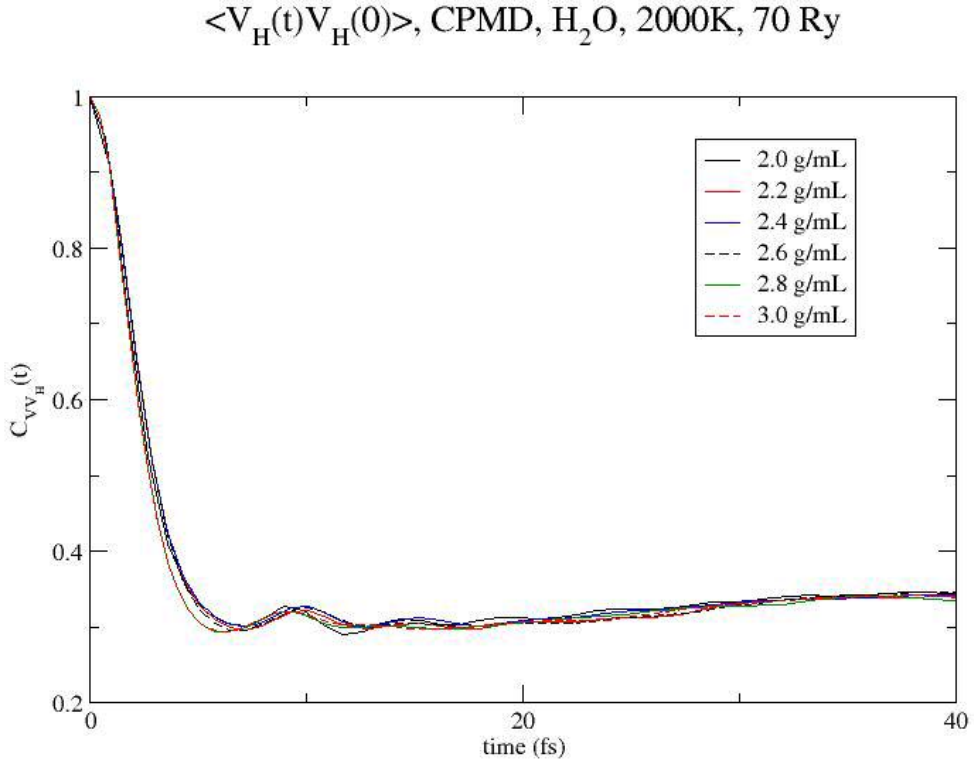



CPMD, g(R_OH), 54 H_2O, 2000 K, 70 Ry
2.0g/mL
2.2g/mL
2.4 g/mL
2.6 g/mL
2.8 g/mL
3.0 g/mL
g(R_OH)
R_OH(m^-10)
0
1
2
3
4
5

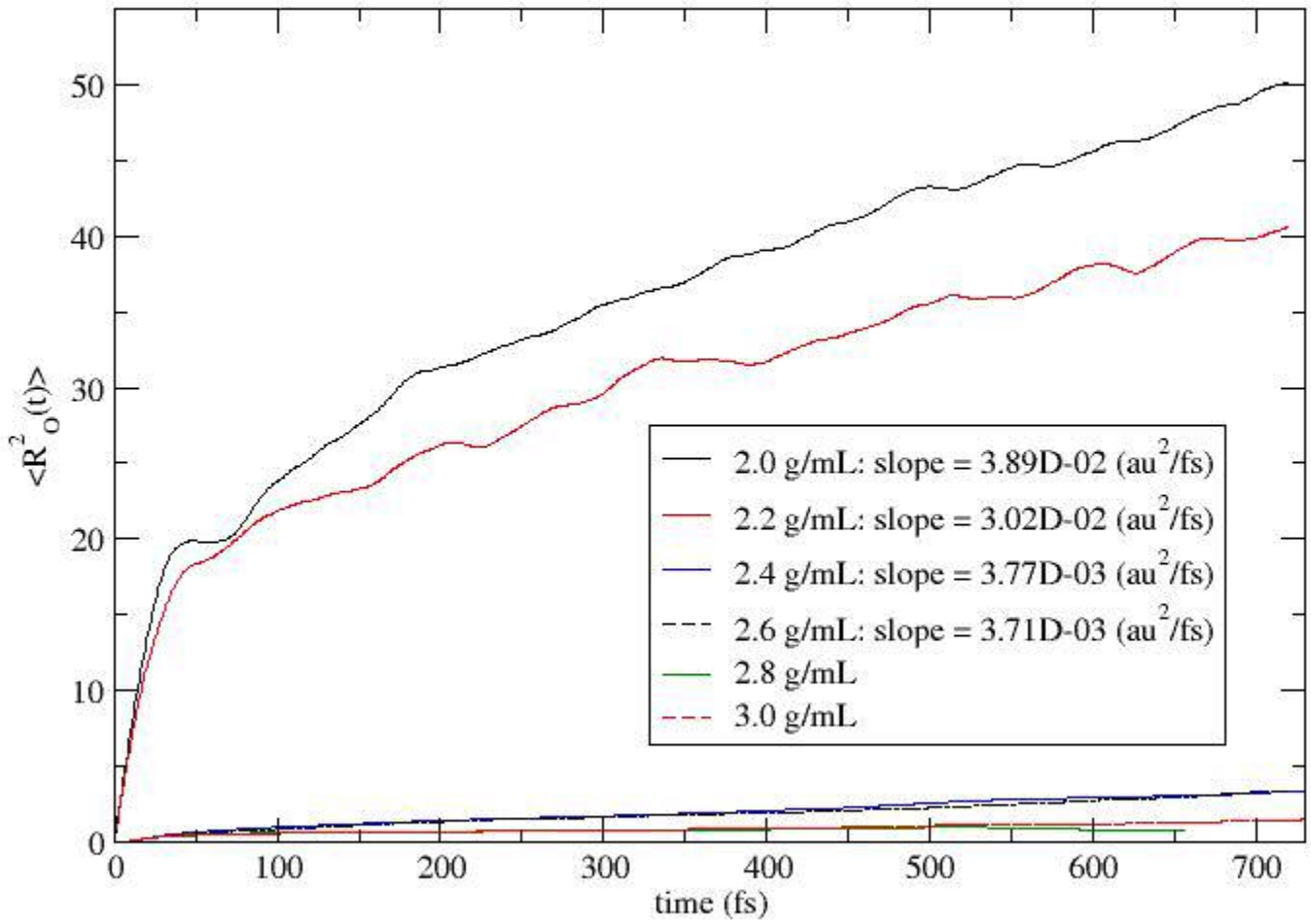

CPMD, g(R_OH), 54 H_2O, 2000 K, 70 Ry
2.6 g/mL
2.8 g/mL
3.0 g/mL
g(R_OH)
R_OH(m^-10)
0
1
2
1
2
3
4


CPMD, g(R_HH), 54 H_2O, 2000K, 70 Ry
2.0g/mL
2.2g/mL
2.4 g/mL
2.6 g/mL
2.8 g/mL
3.0 g/mL
g(R_HH)
R_HH(m^-10)
0
0.5
1
1.5
2
1
2
3
4

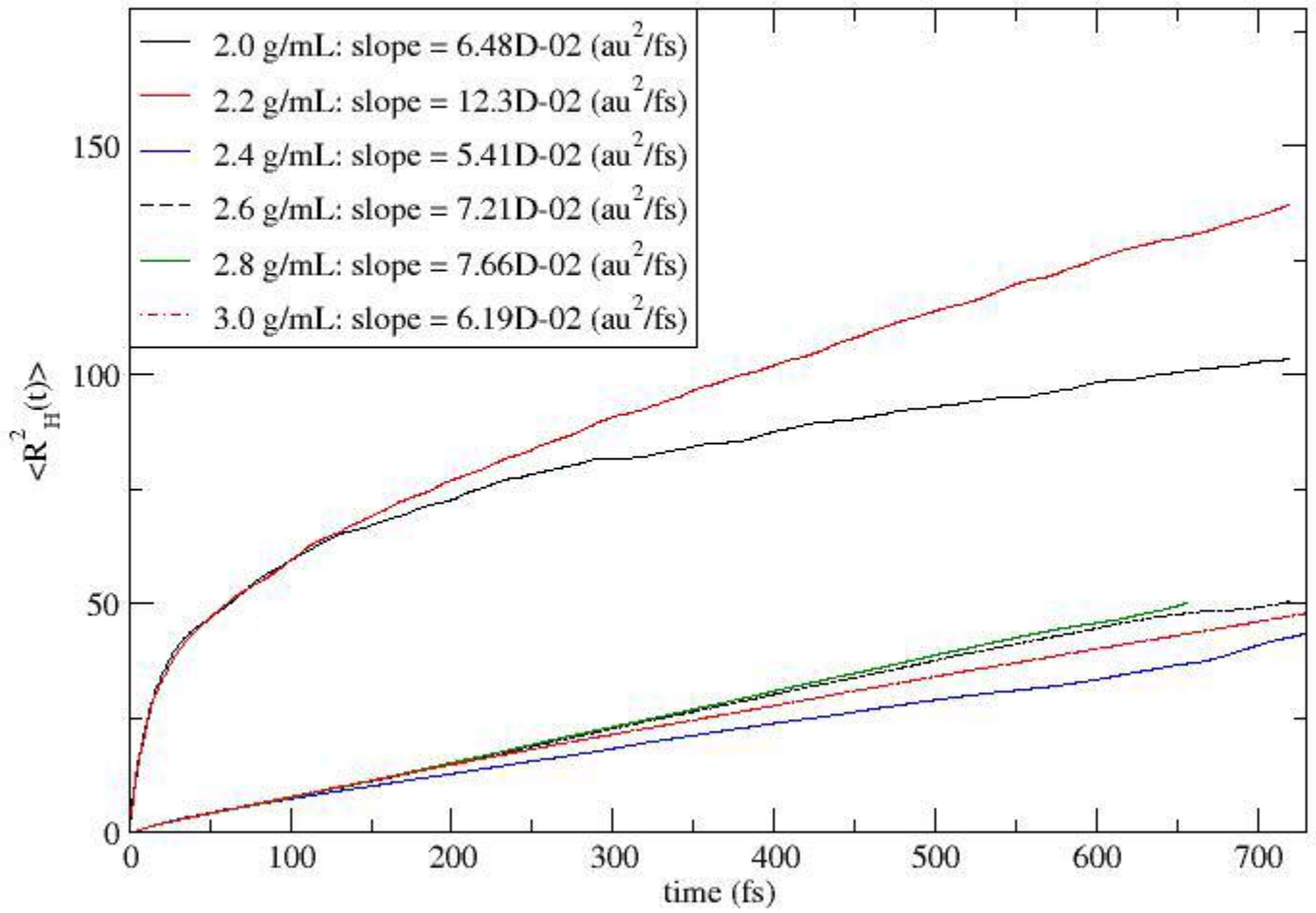

<V_O(t)V_O(0)>, CPMD, 54 H_2O, 2000K, 70 Ry
2.0 g/mL
2.2 g/mL
2.4 g/mL
2.6 g/mL
2.8 g/mL
3.0 g/mL
C_VV_O (t)
time (fs)
0
0.2
0.4
0.6
0.8
1
50


<V_H(t)V_H(0)>, CPMD, H_2O, 2000K, 70 Ry
2.0 g/mL
2.2 g/mL
2.4 g/mL
2.6 g/mL
2.8 g/mL
3.0 g/mL
C_VV_H (t)
time (fs)
0.2
0.4
0.6
0.8
1
0
20
40

CPMD, 54 H_2O, 2000K, 70 Ry

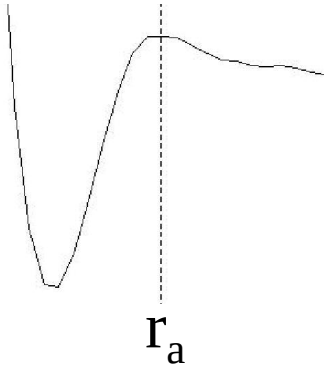


CPMD, 54 H_2O, 2000K, 70 Ry



OH bond dissociation

Define OH bond via free energy surface:



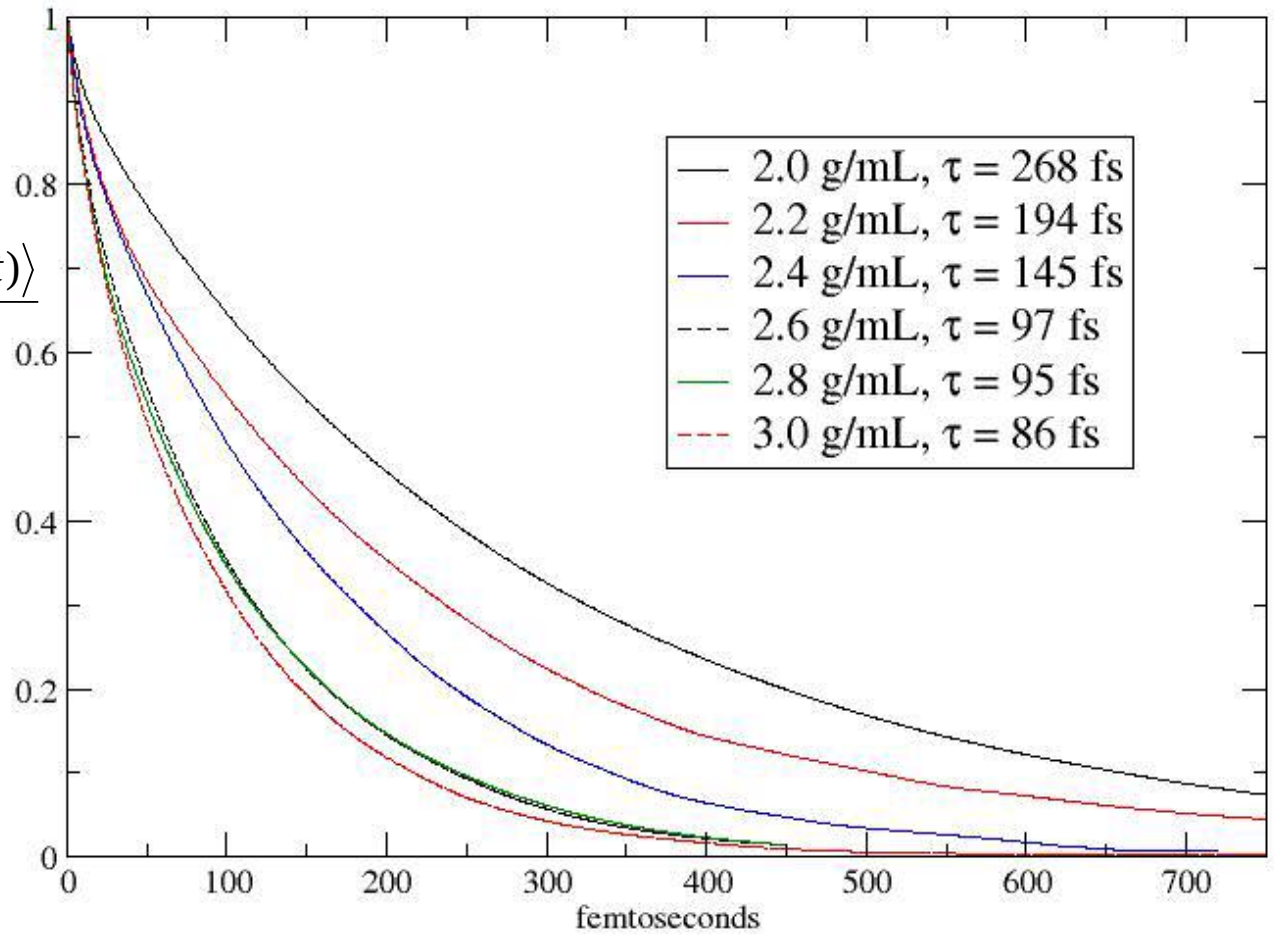
$$\mathrm{H}_a = \begin{cases} 1, r_{OH} \le r_a \\ 0, r_{OH} > r_a \end{cases}$$

$$\left\langle \mathrm{H_a}(0)\,\mathrm{H_a}(t) \right\rangle = \left\langle \mathrm{H_a}(0) \right\rangle e^{-kt}$$

$$\tau = 1/k = \text{lifetime}$$

OH bond lifetimes

$$\frac{\langle H_a(0)\,H_a(t)\rangle}{\langle H_a(0)\rangle}$$



Discussion

- $g(R_{OH})$ shows increased structure with increased density
  - Repeated structure at 2.6 g/cc and above
  - Diminishing but still present first peak
- H diffusion constant (D_H) reaches ‘superionic’ proportions at 2.0 g/cc
  - O atoms do not form lattice until 2.4 g/cc
  - Move much slower than H atoms

Discussion

- Starting to clarify issue of superionic phase
- At ρ>2.4 g/cc, ratio of D_H:D_O > 15:1!
  - Definition of bond is “fuzzy”
- OH bond lifetimes significant, but dissociation is no longer a rare event

Future Work

- 32 H_2O CPMD simulations to re-examine work by Cavazzoni et al.
- Issue of speciation:

$$\langle H_2O \rangle, \langle H_3O^+ \rangle, \langle H^+ \rangle, \langle OH^- \rangle$$

- Investigation of transition states
- Characterization of phase change at 2.4 g/cc

Acknowledgments

- Dr. Larry Fried, LLNL
- Drs. Chris Mundy and Will Kuo, LLNL

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.